

# UNITED STATES ENVIRONMENTAL PROTECTION AGENCY WASHINGTON, D.C. 20460

OFFICE OF PREVENTION, PESTICIDE **AND TOXIC SUBSTANCES** 

# **MEMORANDUM**

Date: 11/30/09

SUBJECT: Pyraclostrobin: Label amendment for the ultra low volume (ULV) aerial

application on Corn and Wheat.

**PC Code:** 099100 **DP Barcodes:** 368042, 368086

**Decision Nos.:** 416934, 416935 **Registration Nos.:** 7969-186, 7969-289

**Petition No.:** N/A **Regulatory Action:** Section 3 Registration

Risk Assessment Type: N/A Case No.: N/A

CAS No.: 175013-18-0 TXR No.: N/A

MRID No.: 47774601 and 47774602 **40 CFR:** 180.582

Ver.Apr.08

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FROM:

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THROUGH:

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TO:

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# **Executive Summary**

Pyraclostrobin has established tolerances ranging from 0.04-23 ppm in/on corn commodities and 0.02-6 ppm in/on wheat commodities. The field trials on corn were conducted using 6 ground applications at ~0.20 lb ai/A/application (max seasonal rate of ~1.2 lb ai/A) with PHI of 7 days (L. Cheng, DP# 281042, 07/26/04). The registered use rate for wheat is 2 ground applications at 0.2 lb ai/A (max seasonal rate of 0.34 lb ai/A) (L. Cheng, DP# 269668, 11/28/01).

BASF Corporation (BASF) currently has two pyraclostrobin end-use products (EPs) Headline® Fungicide (EPA Reg. No. 7969-186) and Headline® Fungicide SC (EPA Reg. No. 7969-289) that are registered for use on corn and wheat. These EPs are 2 lb ai/gal emulsifiable concentrate (EC) and suspension concentrate (SC), respectively. BASF has requested an amended label for these formulations to permit aerial application on corn and wheat using spray volumes as low as 1 gal/A (GPA).

To support this registration, the Agency requested that BASF submit residue bridging data using ground versus aerial application. In response, BASF has submitted residue data from side-by-side field trials on corn and wheat conducted at 1, 2 and 20 GPA spray volumes using the EC formulation and ground equipment. In addition, to support the aerial use, BASF has submitted preliminary model generated deposition profile for aerial application to compare with the ground deposition. However, detailed input and output data for the model simulations as well as application specifications (i.e. nozzles types, operating pressure and boom height) for ground equipment are needed to verify the residue bridging data for aerial application (R. Miller, F. Khan, 11/18/09, DP#s 370130, 370133).

The submitted side-by-side field trial data are adequate and indicate that the results showed that there were no observable differences in the residues of pyraclostrobin between the various application spray volumes on wheat commodities and corn commodities except in corn stover where residues were lower with lower spray volumes. The established tolerances in/on corn and wheat commodities will not be exceeded by the proposed supplemental use. No additional field trial data are required to support the proposed label amendment.

There are adequate storage stability data from previous pyraclostrobin petition submissions (L. Cheng (PP#0F6139), DP# 269668, 11/28/01). These data may be translated in the current submission to validate sample storage conditions and durations. Pyraclostrobin residues were found to be reasonably stable over a wide range of commodities under frozen storage conditions for up to 25 months.

#### Regulatory Recommendations and Residue Chemistry Deficiencies

Pending submission of the detailed input and output data to Environmental Fate and Effects Division (EFED) and provided that the data are adequate, HED recommends for a conditional registration for the requested uses of pyraclostrobin on corn and wheat. The conditional registration status may be converted to unconditional status when the requested data becomes available and is deemed adequate. There are no residue chemistry issues that would preclude granting registration for the requested label amendment (Headline® Fungicide (EPA Reg. No.

7969-186 and Headline® Fungicide SC (EPA Reg. No. 7969-289) to allow aerial application of pyraclostrobin with spray volume as low as 1 GPA in corn and wheat.

### Background

Pyraclostrobin belongs to the strobilurin class of fungicides. Strobilurins are synthetic analogs of a natural antifungal substance which inhibits spore germination and mycelial growth and sporulation of the fungus on the leaf surface. The fungicide is currently registered to BASF for use on a variety of field, vegetable, fruit, and nut crops. Permanent tolerances are established [40 CFR §180.582(a)(1)] and are expressed in terms of the combined residues of the fungicide pyraclostrobin (carbamic acid, [2-[[[1-(4-chlorophenyl)-1*H*- pyrazol-3-yl]oxy]methyl]phenyl] methoxy-, methyl ester) and its desmethoxy metabolite (methyl *N*-[[[1-(4-chlorophenyl)-1*H*-pyrazol-3-yl]oxy]methyl]phenyl carbamate), expressed as parent compound. The established tolerances for plant commodities range from 0.02 ppm in/on wheat grain to 29 ppm in/on leafy vegetables, except *Brassica*. Pyraclostrobin has an established tolerance in/on corn commodities ranging from 0.04-23 ppm and 0.02-6 ppm in/on wheat grain commodities. Currently, pyraclostrobin may be foliarly applied to corn at a maximum seasonal rate of 1.18 lb ai/A and a pre-harvest interval (PHI) of 7 days and to wheat at a maximum seasonal rate of 0.34 lb ai/A.

The chemical structure and nomenclature of pyraclostrobin are presented in Table 1. The physicochemical properties of the technical grade of pyraclostrobin are presented in Table 2.

TABLE 1. Test Comp	ound Nomenclature.
Compound	CI N OCH3
Common name	Pyraclostrobin
Company experimental name	BAS 500 F
IUPAC name	methyl N-{2-[1-(4-chlorophenyl)-1H-pyrazol-3-yloxymethyl]phenyl}(N-methoxy) carbamate
CAS name	methyl [2-[[[1-(4-chlorophenyl)-1 <i>H</i> -pyrazol-3-yl]oxy]methyl]phenyl]methoxycarbamate
CAS registry number	175013-18-0
End-use products (EP)	2 lb ai/gal emulsifiable concentrate formulation (EC; Headline® Fungicide, EPA Reg. No. 7969-186). 2 lb ai/gal suspension concentrate formulation (SC; Headline® Fungicide, EPA Reg. No. 7969-289).

TABLE 2. Physicochemical Properties of Technical Grade Pyraclostrobin.								
Parameter	Value	References <sup>1</sup> (MRID)						
Melting point/range	63.7-65.2° C	45118213						
рH	Not applicable							
Density	1.367 g/cm <sup>3</sup>	45118214						
Water solubility at 20° C	$1.9 \pm 0.17$ mg/L (deionized water, pH 5.8)	45118233						

TABLE 2. Physicochemical	Properties of Technical Grade Pyraclostrobin.	
Parameter	Value	References <sup>1</sup> (MRID)
Solvent solubility	n-heptane (0.37 g/100mL); 2-propanol (3.0 g/100mL); 1-octanol (2.42 g/100mL); olive oil (2.80 g/100m/L); methanol (10.08 g/100mL); >50 g/100mL in acetone, ethyl acetate, acetonitrile, DCM and toluene.	45118228
Vapor pressure	2.6 x 10 <sup>-10</sup> hPa at 20° C	45118214
Dissociation constant, pKa	None (no dissociable moieties)	
Octanol/water partition coefficient, Log(K <sub>OW</sub> ) at room temperature	3.990 mean log Pow; Pow is 9772	45118215
UV/visible absorption spectrum	The structural identity of BAS 500 F was confirmed by NMR and MS spectra. UV molecular extinction (e [1 mol <sup>-1</sup> cm <sup>-1</sup> ]): 2.5x10 <sup>4</sup> at 205 nm; 2.4x10 <sup>4</sup> at 275 nm.	1996/10955 <sup>2</sup>

Product Chemistry data were reviewed by the Registration Division (DP# 269848 and DP# 274191, 5/3/01, 5/15/01, and 6/7/01, S. Malak).

# **Directions for Use**

A summary of the proposed pyraclostrobin end-use products for use on the crops discussed in this document is listed in Table 3. Table 4 presents the summary of the registered crop use patterns.

TABLE 3. Sur	TABLE 3. Summary of Proposed Pyraclostrobin End-Use Products.									
Trade Name	EPA Reg. No.	% ai of Formulation	Formulation Type	Target Crops	Label Date					
Headline® Fungicide	7969-186	23.6%, (2.09 lb ai/gal)	EC	Corn, Wheat	Supplemental label not dated					
Headline® SC Fungicide	7969-289	23.6% (2.08 lb ai/gal)	sc	Corn, Wheat	Supplemental label not dated					

TABLE 4. Summary	of Registered	Use of Pyrac	lostrobin.			
Applic. Timing, Type, and Equip.	Formulation [EPA Reg. No.]	Applic. Rate (lb ai/A) fl oz/A	Max. No. Applic. per Season	Max. Seasonal Applic. Rate (lb ai/A) fl oz/A	PHI (days)	Use Directions and Limitations
	Corn includi	ing field com, po	op corn, sw	eet com, seed pr	oduction	com
Broadcast foliar spray; Ground or aerial	Headline® Fungicide [EPA Reg. No. 7969- 186]/ Headline® SC Fungicide [EPA Reg. No. 7969- 289/	(0.10-0.20) 6-12	NS	(1.18) 72	7	Applications may begin prior to disease development and continue on a 7- to 14-day interval. Use higher rate (0.15-0.2 lb ai/A, 9-12 fl oz/A) when disease pressure is high (Northern leaf blight and Southern leaf blight). The use rate in California is 9-12 fl oz/A. The maximum product rate per season included the combination of in furrow and foliar uses.

<sup>&</sup>lt;sup>2</sup> BASF Document Number.

TABLE 4. Summary	of Registered	Use of Pyrac	lostrobin.			
Applic. Timing, Type, and Equip.	Formulation [EPA Reg. No.]	Applic. Rate (lb ai/A) fl oz/A	Max. No. Applic. per Season	Max. Seasonal Applic. Ra (lb ai/A) fl oz/A	te	Use Directions and Limitations
						adjuvants. Resistance Management: To limit the potential for development of resistance, do not apply more than 1.18 lbs ai/A (=72 fl oz/A/season). In field corn, do not make more than two applications per season. Do not make more than 2 sequential applications before alternating to a labeled nongroup 11 fungicide with a different mode of action.
		Wh	eat and Tri	ticale		1
Broadcast foliar spray; Ground or aerial	Headline® Fungicide [EPA Reg. No. 7969- 186]/ Headline® SC Fungicide [EPA Reg. No. 7969-289/	(0.10-0.15) 6-9	2	(0.29) 18	Apply no later than the beginning of flowering	Apply no later than the beginning of flowering (Feekes 10.5 Zadok's 59).  Applications may begin prior to disease development. For optimum result apply after flag leaf emergence.  Resistance Management: Do not apply more than 0.29 lb ai/A (18 fl oz)/A/season.  Do not make more than 2 applications of Headline or other group 11 fungicides per season.  Do not harvest wheat hay or feed green-chopped wheat within 14 DALA.

#### 860.1500 Crop Field Trials

#### Corn

**DER Reference List** 

47774601.der.doc

BASF has submitted supplemental field trial data for pyraclostrobin (BAS 500 F) on corn. A total of three corn trials were conducted in EPA Region 5 (IL, 2-trials; IA, 1-trial) during the 2008 growing season.

At each test location, an untreated plot (control) and three treated plots were established at each site. The treated plots received two foliar broadcast applications of pyraclostrobin (2 lb ai/gal EC (emulsifiable concentrate); BASF formulation code, BAS 500 00F) at 0.19-0.21 lb ai/A (0.213-0.235 kg ai/ha), with a 6-8 day retreatment interval (RTI), totaling a seasonal rate of 0.39-0.41 lb ai/A (0.437-0.460 kg ai/ha). Applications were initiated when the corn plants were at the silking to blister growth stages (BBCH 61-71). At one site (R080491), two additional broadcast

applications of pyraclostrobin were made to the treated plots at 0.2 lb ai/A (0.224 kg ai/ha) resulting in four sequential applications (two times the maximum allowed per season), with a 7-day RTI, totaling in a seasonal rate of 0.80-0.81 lb ai/A (0.897-0.908 kg ai/ha). The third application at this site was made at BBCH 87 to maturing corn and the fourth application was made 7 days prior to harvest of mature grain and stover (BBCH 89).

The applications were made in approximately 20-21 gal/A (GPA) of water (187-196 L/ha), 2 GPA of water (19-20 L/ha), and 1 GPA of water (9-10 L/ha) using commercial or simulated commercial ground equipment. A crop oil concentrate (COC) was added to the spray mixture for all applications at a rate of 0.5 pt/A.

Corn forage and kernel plus cob with husk removed (K+CWHR) raw agricultural commodity (RAC) samples were harvested from all three sites 6-8 days after the second application, at BBCH 75-79 growth stage (milk stage-R3). The mature grain and stover RAC samples were harvested at normal crop maturity, 7 days after last application (DALA) at the test site in IA.

The residues of pyraclostrobin and its *N*-desmethoxy metabolite, 500M07, previously designated 500M07) in/on corn RAC samples (K+CWHR, forage, grain, and stover) were quantitated using a liquid chromatography/mass spectroscopy/mass spectroscopy (LC/MS/MS) method, BASF analytical method number D9908 (Version II). The validated limit of quantitation (LOQ) was 0.02 ppm for each analyte, for a combined LOQ of 0.04 ppm. Acceptable concurrent method recovery data for corn RAC samples were obtained for each analyte. The method limit of detection (LOD) for each analyte in/on corn RAC samples was 0.004 ppm.

The results from these trials (Forage and K+CWHR) indicate that combined residues of pyraclostrobin were 0.64-3.26 ppm (20 GPA), <0.04-3.37 ppm (2 GPA), and 0.29-2.57 ppm (1 GPA) in/on treated corn forage samples, each harvested 6-8 DALA. Combined residues of pyraclostrobin were below the LOQ (<0.04 ppm) in all treated corn K+CWHR samples.

The results from grain and stover trials indicate that combined residues of pyraclostrobin were below the LOQ in all treated corn grain samples harvested at maturity, 7 DALA. Combined residues of pyraclostrobin in/on stover samples harvested 7 DALA were 3.22 and 3.53 ppm (20 GPA), 2.49 and 2.53 ppm (2 GPA), and 0.55 and 1.68 ppm (1 GPA).

The residues of pyraclostrobin between the various application spray volumes were comparable on all corn RACs except for stover where combined residues averaged 3.38, 2.51, and 1.12 ppm with spray volumes of 20, 2, and 1 GPA, respectively, indicating that residues are lower with lower spray volumes.

The storage interval from collection to extraction ranged from 145-219 days (4.8-7.2 months) for corn RAC samples. Adequate storage stability data are available indicating that both pyraclostrobin and 500M07 are stable in frozen storage for 25 months (L. Cheng, DP# 269668, 11/28/01).

TABLE 5.	Sum	mary (	of Residue Da	ta from	Crop F	ield Trial	s with P	yraclost	robin.		
Commodity	Total	PHI	Analyte					e Levels			
	Applic. Rate	(days)		GPA	n¹	14:-	<del></del>	pm) HAFT <sup>2</sup>	3.4-4!		Cul D.
	(lb a.i./A)			GPA	n -	Min	Max	HAFT	Median (STMdR)	Mean (STMR)	Std. Dev.
Forage	0.39-0.41	6-8	Pyraclostrobin	20	6	0.50	2.68	2.56	0.84	1.32	0.97
			500M07			0.15	0.69	0.64	0.21	0.34	0.23
		-	Total Pyraclostrobin			0.64	3.26	3.20	1.04	1.65	1.21
			Pyraclostrobin	2	6	<0.02	2.72	2.43	0.82	1.09	1.11
			500M07			<0.02	0.65	0.53	0.23	0.26	0.24
			Total Pyraclostrobin			<0.04	3,37	2.96	1.05	1.35	1.35
			Pyraclostrobin	1	6	0.24	2.09	1.76	0.66	0.92	0.70
			500M07			0.05	0.48	0.39	0.19	0.21	0.16
			Total Pyraclostrobin			0.29	2.57	2.15	0.85	1.13	0.86
K+CWHR	0.39-0.41	6-8	Pyraclostrobin	20	6	<0.02	<0.02	<0.02	<0.02	<0.02	N/A <sup>3</sup>
			500M07			<0.02	<0.02	<0.02	<0.02	<0.02	N/A
			Total Pyraclostrobin			<0.04	<0.04	<0.04	<0.04	<0.04	N/A
			Pyraclostrobin	2	6	<0.02	<0.02	<0.02	<0.02	<0.02	N/A
			500M07			<0.02	<0.02	<0.02	<0.02	<0.02	N/A
			Total Pyraclostrobin			<0.04	<0.04	<0.04	<0.04	<0.04	N/A
			Pyraclostrobin	1	6	<0.02	<0.02	<0.02	<0.02	<0.02	N/A
			500M07			<0.02	<0.02	<0.02	<0.02	<0.02	N/A
			Total Pyraclostrobin			<0.04	<0.04	<0.04	<0.04	<0.04	N/A
Grain	0.80-0.81	7	Pyraclostrobin	20	2	<0.02	<0.02	<0.02	<0.02	<0.02	N/A
			500M07			<0.02	<0.02	<0.02	<0.02	<0.02	N/A
			Total Pyraclostrobin			<0.04	<0.04	<0.04	<0.04	<0.04	N/A
			Pyraclostrobin	2	2	<0.02	<0.02	<0.02	<0.02	<0.02	N/A
			500M07			<0.02	<0.02	<0.02	<0.02	<0.02	N/A
			Total Pyraclostrobin			<0.04	<0.04	<0.04	<0.04	<0.04	N/A
			Pyraclostrobin	1	2	<0.02	<0.02	<0.02	<0.02	<0.02	N/A
			500M07			<0.02	<0.02	<0.02	<0.02	<0.02	N/A
			Total Pyraclostrobin			<0.04	<0.04	<0.04	<0.04	<0.04	N/A
Stover	0.80-0.81	7	Pyraclostrobin	20	2	2.47	2.76	2.62	2.62	2.62	N/A
			500M07			0.76	0.77	0.77	0.77	0.77	N/A
			Total Pyraclostrobin			3.22	3.53	3.38	3.38	3.38	N/A
			Pyraclostrobin	2	2	2.13	2.16	2.15	2.15	2.15	N/A
			500M07			0.36	0.38	0.37	0.37	0.37	N/A
			Total Pyraclostrobin			2.49	2.53	2.51	2.51	2.51	N/A
			Pyraclostrobin	1	2	0.45	1.44	0.95	0.95	0.95	N/A
			500M07			0.09	0.24	0.17	0.17	0.17	N/A

TABLE 5.	Sum	Summary of Residue Data from Crop Field Trials with Pyraclostrobin.									
Commodity	Total Applic.	PHI (days)	Analyte					ie Levels opm)			
	Rate (lb a.i./A)								Std. Dev.		
			Total Pyraclostrobin			0.55	1,68	1.12	1.12	1,12	N/A

<sup>&</sup>lt;sup>1</sup> n = number of individual specimens

Conclusions: The submitted data for corn are adequate to support the petitioner's request for an amended registration (i.e., permit 1 GPA spray volume for aerial application). The residues of pyraclostrobin between the various application spray volumes were comparable on all corn RACs except for stover where combined residues averaged 3.38, 2.51, and 1.12 ppm with spray volumes of 20, 2, and 1 GPA, respectively, indicating that residues are lower with lower spray volumes. Combined residues of pyraclostrobin were 0.64-3.26 ppm (20 GPA), <0.04-3.37 ppm (2 GPA), and 0.29-2.57 ppm (1 GPA) in/on treated corn forage samples, each harvested 6-8 DALA. Combined residues of pyraclostrobin were below the LOQ (<0.04 ppm) in all treated corn K+CWHR samples. Combined residues of pyraclostrobin were below the LOQ in all treated corn grain samples harvested at maturity, 7 DALA. Combined residues of pyraclostrobin in/on stover samples harvested 7 DALA were 3.22 and 3.53 ppm (20 GPA), 2.49 and 2.53 ppm (2 GPA), and 0.55 and 1.68 ppm (1 GPA). The combined residues of pyraclostrobin and its metabolite 500M07 did not exceed the registered tolerance of 0.1 ppm on corn, field, grain; 5 ppm on corn, field, forage; 17 ppm on corn, field, stover; and 0.04 on corn, sweet, kernel plus cob with husk removed following two applications of the 2.0 lb ai/gal EC formulation of pyraclostrobin reflecting a PHI of 7 days.

#### Wheat

DER Reference List 47

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BASF has submitted supplemental field trial data for pyraclostrobin (BAS 500 F) on wheat. A total of three field trials were conducted in EPA Regions 5 (ND, 2 trials) and 11 (WA, 1 trial) during the 2008 growing season.

At each test location, an untreated plot (control) and three treated plots were established at each site. The treated plots received two foliar broadcast applications of pyraclostrobin (2 lb ai/gal EC; BASF formulation code, BAS 500 00F) at 0.15-0.16 lb ai/A (0.168-0.179 kg ai/ha), with a 7 day RTI, totaling a seasonal rate of 0.30-0.31 lb ai/A (0.336-0.347 kg ai/ha). Applications were targeted at growth stages BBCH 37-39 (ND trials) and Feekes 8 (WA), approximately three weeks prior to the harvest of forage (green chop) and hay samples.

The applications were made in 20 (GPA) of water (187 L/ha), 2 GPA of water (19 L/ha), and 1 (0.97-1.1) GPA of water (9.1-10 L/ha) using commercial or simulated commercial ground equipment. A COC, Agri-Dex, was added to the spray mixture for all applications at a rate of 0.5 pt/A.

Wheat forage (green chop) and hay RAC samples were harvested 14-15 DALA when the crop was at the green chop stage (BBCH 61-75) at all three trial sites. Grain and straw samples were

<sup>&</sup>lt;sup>2</sup> HAFT = Highest Average Field Trial based on combined residues

<sup>&</sup>lt;sup>3</sup> N/A = Not applicable

harvested at maturity at the one trial site, at 69 DALA (BBCH 89).

The residues of pyraclostrobin (and its desmethoxy metabolite, 500M07, formerly designated 500M07) in/on wheat RAC samples (forage, hay, grain and straw) were quantitated using a LC/MS/MS method, BASF analytical method number D9908 (Version II). Acceptable concurrent method recovery data for wheat RAC samples were obtained for each analyte. The validated LOQ for residues of pyraclostrobin and 500M07 in/on wheat RAC samples was 0.02 ppm each (0.04 ppm combined). The LOD for each analyte in/on wheat RAC samples was 0.004 ppm.

The results from these trials (forage, hay, grain and straw) indicate that combined residues of pyraclostrobin were 0.31-0.68 ppm (20 GPA), 0.19-0.70 ppm (2 GPA), and 0.30-0.71 ppm (1 GPA) in/on wheat forage samples; 1.00-2.00 ppm (20 GPA), 1.23-2.30 ppm (2 GPA), and 1.24-2.34 ppm (1 GPA) in/on wheat hay, each harvested 14 DALA. Combined residues of pyraclostrobin were 0.11 and 0.09 ppm (20 GPA), 0.15 and 0.14 ppm (2 GPA), and 0.22 and 0.15 ppm (1 GPA) in/on straw samples and were below the LOQ (<0.04 ppm) in all grain samples, each harvested at maturity.

The residues of pyraclostrobin between the various application spray volumes were comparable on all wheat RACs.

The storage interval from collection to extraction ranged from 154-222 days (5.1-7.3 months) for wheat samples. Adequate storage stability data are available indicating that both pyraclostrobin and 500M07 are stable in frozen storage for 25 months.

TABLE 6.	Sum	mary (	of Residue Data from Crop Field Trials with Pyraclostrobin.									
Commodity	Total Applic.	PHI (days)	Analyte	Residue Levels (ppm)								
	Rate (lb a.i./A)			GPA	n¹	Min	Max	HAFT <sup>2</sup>	Median (STMdR)	Mean (STMR)	Std. Dev.	
Forage	0.30	14-15	Pyraclostrobin	20	6	0.24	0.57	0.52	0.34	0.37	0.13	
			500M07			0.07	0.11	0.11	0.10	0.09	0.02	
			Total Pyraclostrobin			0.31	0.68	0.62	0.45	0.46	0.14	
			Pyraclostrobin	2	6	0.15	0.56	0.52	0.46	041	0.14	
			500M07			0.04	0.15	0.14	0.11	0.10	0.04	
			Total Pyraclostrobin			0.19	0.70	0.65	0.57	0.51	0.18	
			Pyraclostrobin	1	6	0.23	0.57	0.56	0.55	0.46	0.15	
			500M07			0.07	0.15	0.14	0.11	0.11	0.03	
			Total Pyraclostrobin			0.30	0.71	0.70	0.67	0.57	0.18	
Hay	0.30	14-15	Pyraclostrobin	20	6	0.82	1.73	1.64	1.21	1.25	0.35	
			500M07			0.19	0.47	0.47	0.38	0.35	0.12	
			Total Pyraclostrobin			1.01	2.20	2.11	1.59	1.60	0.46	
		1	Pyraclostrobin	2	6	0.96	1.80	1.64	1.17	1.26	0.32	
			500M07			0.25	0.51	0.47	0.38	0.37	0.10	
			Total Pyraclostrobin			1.23	2.30	2.12	1.55	1.63	0.42	

TABLE 6.			f Residue Da	ta from	Crop Fi	eld Trial					
Commodity	Total Applic.	PHI (days)	Analyte					ue Levels ppm)			
	Rate (lb a.i./A)			GPA	n <sup>t</sup>	Min	Max	HAFT <sup>2</sup>	Median (STMdR)	Mean (STMR)	Std. Dev
			Pyraclostrobin	i	6	0.99	1.85	1.76	1.43	1.40	0.33
			500M07			<0.24	0.49	0.48	0.40	0.37	0.11
			Total Pyraclostrobin			1.24	2.34	2.23	1.83	1.78	0.44
Grain	0.30	69	Pyraclostrobin	20	2	<0.02	<0.02	<0.02	<0.02	<0.02	N/A <sup>3</sup>
	ļ		500M07			<0.02	<0.02	<0.02	<0.02	<0.02	N/A
			Total Pyraclostrobin			<0.04	<0.04	<0.04	<0.04	<0.04	N/A
			Pyraclostrobin	2	2	<0.02	<0.02	<0.02	<0.02	<0.02	N/A
			500M07			<0.02	<0.02	<0.02	<0.02	<0.02	N/A
			Total Pyraclostrobin			<0.04	<0.04	<0.04	<0.04	<0.04	N/A
			Pyraclostrobin	1	2	<0.02	<0.02	<0.02	<0.02	<0.02	N/A
			500M07			<0.02	<0.02	<0.02	<0.02	<0.02	N/A
			Total Pyraclostrobin			<0.04	<0.04	<0.04	<0.04	<0.04	N/A
Straw	0.30	69	Pyraclostrobin	20	2	0.06	0.08	0.07	0.07	0.07	N/A
		<u> </u>	500M07			0.03	0.04	0.03	0.03	0.03	N/A
			Total Pyraclostrobin			0.09	0.11	0.10	0.10	0.10	N/A
			Pyraclostrobin	2	2	0.10	0.11	0.10	0.10	0.10	N/A
			500M07			0.04	0.04	0.04	0.04	0.04	N/A
			Total Pyraclostrobin			0.14	0.15	0.15	0.15	0.15	N/A
			Pyraclostrobin	1	2	0.11	0.16	0.14	0.14	0.14	N/A
			500M07			0.04	0.05	0.05	0.05	0.05	N/A
			Total Pyraclostrobin			0.15	0.21	0.19	0.19	0.19	N/A

In = number of individual specimens

Conclusions: The submitted data for wheat are adequate to support the petitioner's request for an amended registration (i.e., permit 1 GPA spray volume for aerial application). The residues of pyraclostrobin between the various application spray volumes were comparable on all wheat RACs. The combined residues ranged from 0.31-0.68 ppm (20 GPA), 0.19-0.70 ppm (2 GPA), and 0.30-0.71 ppm (1 GPA) in/on wheat forage samples; 1.00-2.00 ppm (20 GPA), 1.23-2.30 ppm (2 GPA), and 1.24-2.34 ppm (1 GPA) in/on wheat hay, each harvested 14 DALA. Combined residues of pyraclostrobin were 0.11 and 0.09 ppm (20 GPA), 0.15 and 0.14 ppm (2 GPA), and 0.22 and 0.15 ppm (1 GPA) in/on straw samples and were below the LOQ (<0.04 ppm) in all grain samples, each harvested at maturity. The combined residues of pyraclostrobin and its metabolite 500M07 did not exceed the registered tolerance of 0.2 ppm in/on wheat, grain, 6 ppm on wheat, hay; and 8.5 ppm on wheat, straw following two applications of the 2.0 lb ai/gal EC formulation of pyraclostrobin reflecting a PHI of 7 days.

<sup>&</sup>lt;sup>2</sup> HAFT = Highest Average Field Trial based on combined residues

 $<sup>^{3}</sup>$  N/A = Not applicable

#### References

DP#s:

269668, 272771, 272789, 274095, 274192, 274471, 274957, 275843, and 278429

Subject:

PP#0F06139. Pyraclostrobin on Various Crops: Bananas (import), Barley,

Berries, Bulb Vegetables, Citrus Fruits, Cucurbit Vegetables, Dried Shelled Pea & Bean (except Soybean), Fruiting Vegetables, Grapes, Grass, Peanut, Pistachio, Root Vegetables (except Sugar Beet), Rye, Snap Beans, Stone Fruits, Strawberry, Sugar Beet, Tree Nuts, Tuberous and Corm Vegetables, and Wheat. Review of

Analytical Methods and Residue Data. EPA File Symbols:

From:

L. Cheng

To:

C. Giles-Parker/J. Bazuin

Dated:

11/28/01

MRIDs:

45118428-451184-37, 45118501-45118512, 45118514-45118537, 45118601-

45118625, 45160501, 45272801, 45274901, 45321101, 45367501, 45399401, and

45429901

DP#:

278044

Subject:

PP# 0F06139. PC Code 099100. Pyraclostrobin. Outcome of the HED

Metabolism Assessment Review Committee (MARC) Meeting Held on

September 20, 2001.

From:

L. Cheng

To:

Y. Donovan

Dated:

10/09/01

MRIDs:

None

DP#:

269850

Subject:

PP# 0F06139. Pyraclostrobin (BAS 500F) in or on Various Crops. Request for

Tolerance Method Validation (TMV) Trial.

From:

L. Cheng

To:

F. D. Griffith, Jr.

Dated:

11/8/00

MRIDs:

45118505, 45118504, 45118509, 45118510, 45118501, 45118503, 45118507,

45118514

DP Barcodes: D281042, D286732, D287729, D288459, D290342, D290343, D290369,

D292440, D293088, D293684, D295893, and D298178

Subject:

Pyraclostrobin. PP#3F06581, 2F06431, 2E6473, 3E6548, 3E6553, 3E6774, and

2F06139. Petitions for the establishment of permanent tolerances to allow uses on

corn (field, sweet, and pop), hops, mint, pome fruits, edible-podded legume vegetables, succulent peas, sunflower, Brassica leafy greens, soybeans, succulent beans, broccoli, cabbage, lettuce (head and leaf), spinach, celery, turnip greens, and the import commodities mango and papaya. Application for amended Section 3 registration for citrus (reduced PHI). Petitioner's response to data deficiencies identified in PP#0F06139 regarding storage stability data, dried shelled peas and

beans (reduced PHI), and uses on dry and succulent peas. Summary of Analytical

Chemistry and Residue Data.

From:

L. Cheng

DP#: 368042

Pyraclostrobin

To:

C. Giles-Parker/J. Bazuin

Dated:

7/26/04

MRIDs:

45596211, 45623406, 45623407, 45623408, 45623410, 45645801, 45645802,

45645803, 45645804, 45702901, 45765401, 45832001, 45858801, 45858802,

45903601, 45903602, 46033901-04, 46084401-04, 46109101, 46109102

Template Version November 2003

**Primary Evaluator** Meheret Negussie, Chemist

Risk Assessment Branch III

Health Effects Division (7509P)

Heheret Negustre

Approved by Stephen Funk, Senior Science Advisor

Date: 11/30/09

Date: 11/05/09

Risk Assessment Branch III Health Effects Division (7509P)

### **STUDY REPORTS:**

47774602 Wyatt, D. (2009) Magnitude of the Residue of Pyraclostrobin in or on Wheat Raw Agricultural Commodities Following Applications of BAS 500 00F with Various Application Spray Volumes. BASF Study Number 354771. BASF Reg. Doc. No. 2009/7000170. Unpublished study prepared by the Carringers, Inc., 130 p.

# **EXECUTIVE SUMMARY:**

BASF Corporation (BASF) has submitted supplemental field trial data for pyraclostrobin (BAS 500 F) on wheat. A total of three trials were conducted in EPA Regions 5 (ND, 2 trials) and 11 (WA, 1 trial) during the 2008 growing season.

At each test location, an untreated plot (control) and three treated plots were established at each site. The treated plots received two foliar broadcast applications of pyraclostrobin (2 lb ai/gal EC (emulsifiable concentrate); BASF formulation code, BAS 500 00F) at 0.15-0.16 lb ai/A (0.168-0.179 kg ai/ha), with a 7 day retreatment interval (RTI), totaling a seasonal rate of 0.30-0.31 lb ai/A (0.336-0.347 kg ai/ha). Applications were targeted at growth stages BBCH 37-39 (ND trials) and Feekes 8 (WA), approximately three weeks prior to the harvest of forage (green chop) and hay samples.

The applications were made in 20 gal/A (GPA) of water (187 L/ha), 2 GPA of water (19 L/ha), and 1 (0.97-1.1) GPA of water (9.1-10 L/ha) using commercial or simulated commercial ground equipment. A crop oil concentrate (COC), Agri-Dex, was added to the spray mixture for all applications at a rate of 0.5 pt/A.

Wheat forage (green chop) and hay raw agricultural commodity (RAC) samples were harvested 14-15 days after the last application (DALA) when the crop was at the green chop stage (BBCH 61-75) at all three trial sites. Grain and straw samples were harvested at maturity at the one trial site, at 69 DALA (BBCH 89).

The residues of pyraclostrobin (and its desmethoxy metabolite, 500M07, formerly designated

BF 500-3) in/on wheat RAC samples (forage, hay, grain and straw) were quantitated using a liquid chromatography/mass spectroscopy/mass spectroscopy LC/MS/MS method, BASF analytical method number D9908 (Version II). Acceptable concurrent method recovery data for wheat RAC samples were obtained for each analyte. The validated limit of quantitation (LOQ) for residues of pyraclostrobin and 500M07 in/on wheat RAC samples was 0.02 ppm each (0.04 ppm combined). The method limit of detection (LOD) for each analyte in/on wheat RAC samples was 0.004 ppm.

The results from these analyses (forage, hay, grain and straw) indicate that combined residues of pyraclostrobin were 0.31-0.68 ppm (20 GPA), 0.19-0.70 ppm (2 GPA), and 0.30-0.71 ppm (1 GPA) in/on wheat forage samples; 1.00-2.00 ppm (20 GPA), 1.23-2.30 ppm (2 GPA), and 1.24-2.34 ppm (1 GPA) in/on wheat hay, each harvested 14 DALA. Combined residues of pyraclostrobin were 0.11 and 0.09 ppm (20 GPA), 0.15 and 0.14 ppm (2 GPA), and 0.22 and 0.15 ppm (1 GPA) in/on straw samples and were below the LOQ (<0.04 ppm) in all grain samples, each harvested at maturity.

The residues of pyraclostrobin between the various application spray volumes were comparable on all wheat RACs.

The storage interval from collection to extraction ranged from 154-222 days (5.1-7.3 months) for wheat samples. Adequate storage stability data are available indicating that both pyraclostrobin and BF 500-3 are stable in frozen storage for up to 25 months (L. Cheng, DP# 269668, 11/28/01).

#### STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the field trial residue data are classified as scientifically acceptable. The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document DP# 368042.

## **COMPLIANCE:**

Signed and dated Good Laboratory Practice (GLP), Quality Assurance and Data Confidentiality statements were provided. No deviations from regulatory requirements were reported which would have an impact on the validity of the study.

#### A. BACKGROUND INFORMATION

Pyraclostrobin belongs to the strobilurin class of fungicides. Strobilurins are synthetic analogs of a natural antifungal substance which inhibits spore germination, mycelial growth, and sporulation of the fungus on the leaf surface. The fungicide is currently registered to BASF for use on a variety of field, vegetable, fruit, and nut crops. Permanent tolerances are established [40 CFR §180.582(a)(1)] for the combined residues of pyraclostrobin and its desmethoxy metabolite (BF 500-3), expressed as parent, in/on numerous plant commodities at levels ranging from 0.02



ppm in/on wheat grain to 29 ppm in/on leafy vegetables, except *Brassica*. BASF has submitted label amendments of Headline® Fungicide (EPA Reg. No. 7969-186) and Headline® SC Fungicide (EPA Reg. No. 7969-289) to add aerial application at spray volumes down to 1 GPA in wheat.

The chemical structure and nomenclature of pyraclostrobin are presented in Table A.1. The physicochemical properties of the technical grade of pyraclostrobin are presented in Table A.2.

TABLE A.1. Test Comp	ound Nomenclature.
Compound	CI—NNOCH3
Common name	Pyraclostrobin
Company experimental name	BAS 500 00F
IUPAC name	methyl N-{2-[1-(4-chlorophenyl)-1H-pyrazol-3-yloxymethyl]phenyl}(N-methoxy) carbamate
CAS name	methyl [2-[[[1-(4-chlorophenyl)-1 <i>H</i> -pyrazol-3-yl]oxy]methyl]phenyl]methoxycarbamate
CAS registry number	175013-18-0
End-use products (EP)	2 lb ai/gal emulsifiable concentrate formulation (EC; Headline® Fungicide, EPA Reg. No. 7969-186). 2 lb ai/gal suspension concentrate formulation (SC; Headline® SC Fungicide, EPA Reg. No. 7969-289).

Parameter	Value	References (MRID)		
Melting point/range	63.7-65.2° C	45118213		
pH	Not applicable			
Density	1.367 g/cm <sup>3</sup>	45118214		
Water solubility at 20° C	1.9 ± 0.17 mg/L (deionized water, pH 5.8)	45118233		
Solvent solubility	n-heptane (0.37 g/100mL); 2-propanol (3.0 g/100mL); 1-octanol (2.42 g/100mL); olive oil (2.80 g/100m/L); methanol (10.08 g/100mL); >50 g/100mL in acetone, ethyl acetate, acetonitrile, DCM and toluene.	45118228		
Vapor pressure	2.6 x 10 <sup>-10</sup> hPa at 20° C	45118214		
Dissociation constant, pK <sub>a</sub>	None (no dissociable moieties)			
Octanol/water partition coefficient, Log(K <sub>OW</sub> ) at room temperature	3.990 mean log Pow; Pow is 9772	45118215		
UV/visible absorption spectrum	The structural identity of BAS 500 F was confirmed by NMR and MS spectra, UV molecular extinction (e [1 mol <sup>-1</sup> cm <sup>-1</sup> ]): 2.5x10 <sup>4</sup> at 205 nm; 2.4x10 <sup>4</sup> at 275 nm.	1996/10955 <sup>2</sup>		

Product Chemistry data were reviewed by the Registration Division (DP#s 269848 and 274191, 5/3/01, 5/15/01, and 6/7/01, S. Malak).

BASF registration Document Number.



#### B. EXPERIMENTAL DESIGN

At each test location, an untreated plot and three treated plots were established to determine residues in side-by-side comparisons using application spray volumes of 20, 2, and 1 GPA. The treated plots received two foliar broadcast applications of an EC formulation of pyraclostrobin (2 lb ai/gal EC) at 0.15-0.16 lb ai/A (0.168-0.179 kg ai/ha), with a 7 day RTI, totaling a seasonal rate of 0.30-0.31 lb ai/A (0.336-0.347 kg ai/ha). Applications were targeted at growth stages BBCH 37-39 (ND trials) and Feekes 8 (WA), approximately three weeks prior to the harvest of forage (green chop) and hay samples.

The applications were made in 20 gal/A (GPA) of water (187 L/ha), 2 GPA of water (19 L/ha), and 1 (0.97-1.1) GPA of water (9.1-10 L/ha) using commercial or simulated commercial ground equipment. A COC, Agri-Dex, was added to the spray mixture for all applications at a rate of 0.5 pt/A.

Wheat forage (green chop) and hay raw agricultural commodity (RAC) samples were harvested 14-15 days after the last application (DALA) when the crop was at the green chop stage (BBCH 61-75) at all three trial sites. Grain and straw samples were harvested at maturity at the one trial site, at 69 DALA (BBCH 89).

# **B.1.** Study Site Information

Trial site conditions are presented in Table B.1.1. Study site information was provided, and weather data (temperature and rainfall) were compared to historical data (10 year average). Information on maintenance pesticides and fertilizers was also provided for each site.

TABLE B.1.1 Trial Site Condition	ns.							
Trial Identification (City, State/Year)	Soil characteristics							
	Туре	%OM	pН	CEC meq/g				
R080595 (Northwood, ND/2008)	Loam	4.0	7.3	25.8				
R080596 (Northwood, ND/2008)	Loam	5.3	7.6	23.2				
R080597 (Ephrata, WA/2008)	Sandy Loam	1.3	7.4	12.6				

Location	EP <sup>1</sup>	Application								
(City, State/Year); Trial ID		Treatment No.	Method/Timing <sup>2</sup>	Volume GPA <sup>3</sup> (L/ha) <sup>4</sup>	Rate lb a.i./A (kg a.i./ha)	RTI <sup>5</sup> days	Total Rate lb a.i./A (kg a.i./ha)	Adjuvants		
(Northwood,	Headline®	2	Foliar Broadcast/BBCH 39	20 (187)	0.15 (0.168)	NA	0.30	Agri-Dex		
ND/2008);	Fungicide	2	Foliar Broadcast/BBCH 58			7	(0.336)	0.5 pt/A		
R080595	2 lb ai/gal	3	Foliar Broadcast/BBCH 39	2.0 (19)	0.15 (0.168)	NA	0.30	}		
	EC	3	Foliar Broadcast/BBCH 58	1		7	(0.336)			
		4	Foliar Broadcast/BBCH 39	1.1 (10)	0.15-0.16	NA	0.31	1		



Location	EP1		AĮ	plication				Tank Mix/
(City, State/Year); Trial ID		Treatment Method/Timing <sup>2</sup> No.		Volume GPA <sup>3</sup> (L/ha) <sup>4</sup>	Rate lb a.i./A (kg a.i./ha)	RTI <sup>5</sup> days	Total Rate lb a.i./A (kg a.i./ha)	Adjuvants
		4	Foliar Broadcast/BBCH 58	1.0 (9)	(0.168- 0.179)	7	(0.347)	
(Northwood,	ND/2008); Fungicide	2	Foliar Broadcast/BBCH 37	20 (187)	0.15 (0.168)	NA	0.30	Agri-Dex
ND/2008);		2	Foliar Broadcast/BBCH 45	1		7	(0.336)	0.5 pt/A
R080596	2 lb ai/gal EC	3	Foliar Broadcast/BBCH 37	2.0 (19)	0.15 (0.168)	NA	0.30	1
	EC	3	Foliar Broadcast/BBCH 45	1 ` ´		7	(0.336)	
		4	Foliar Broadcast/BBCH 37	1.0 (9)	0.15 (0.168)	NA	0.30	
		4	Foliar Broadcast/BBCH 45			7	(0.336)	
(Ephrata,	Headline®	2	Foliar Broadcast/Feeks 8	20 (187)	0.15 (0.168)	NA	0.30	Agri-Dex
WA/2008);	Fungicide	2	Foliar Broadcast/Feeks 10			7	(0.336)	0.5 pt/A
R080597	2 lb ai/gal	3	Foliar Broadcast/Feeks 8	2.0 (19)	0.15 (0.168)	NΑ	0.30	]
•	EC	3	Foliar Broadcast/Feeks 10			7	(0.336)	
•		4	Foliar Broadcast/Feeks 8	1.0 (9)	0.15 (0.168)	NA	0.30	
		4	Foliar Broadcast/Feeks 10	1		7	(0.336)	

EP = End-use Product

<sup>&</sup>lt;sup>5</sup> RTI = Retreatment Interval

TABLE B.1.3. Trial Number	rs and Geographical Locations.	
	•	Wheat
NAFTA Growing Zones	Submitted	Requested
1		
1A		
2		1
3		
4		1
5	2	
5A		
5B		
6		1
7		5
7A		
8		6
9		
10		· · · · · · · · · · · · · · · · · · ·
11	1	1
12	·	
13		
14		
15		
16		
17		
18		

<sup>&</sup>lt;sup>2</sup> Timing interval in days from application to the time of harvest (forage and hay); crop maturity (grain and straw)

<sup>2</sup> BBCH = Monograph Growth Stages of Plants

<sup>3</sup> GPA = Gallons per Acre

<sup>4</sup> L/ha = Liters/hectare



TABLE B.1.3. Trial Number	rs and Geographical Locations.						
	Wheat						
NAFTA Growing Zones	Submitted	Requested					
19							
20							
21							
Total	3	20					

Justification for the number of side-by-side bridging trials was discussed with EPA officials prior to the start of the study (Rick Loranger, November 2007).

# **B.2.** Sample Handling and Preparation

Single control and duplicate treated samples were collected from each test site. All wheat RAC samples were placed in freezers within 1.17 hours after collection from the field. All samples were maintained frozen at the field facilities and were shipped 9-34 days later by ACDS freezer truck to the analytical laboratory, BASF Agricultural Research Center (ARC) (Research Triangle Park, NC).

All wheat RAC samples were received frozen from the field and were stored in a freezer (<-5°C) at BASF ARC. Samples were homogenized (with dry ice) and were stored frozen in plastic bags prior to analysis. All processed samples were stored frozen until used for fortification and/or analysis.

# **B.3.** Analytical Methodology

The wheat RAC samples (forage, hay, grain, and straw) were analyzed for residues of pyraclostrobin using BASF Analytical Method Number D9908 (Version II), entitled "Method for Determination of BAS 500 F, BF 500-3, and BAS 510 F Residues in Plant Matrices using LC/MS/MS" (Reference 1).

Briefly, wheat samples ~5g were extracted with methanol:water:2N HCl (70:25:5, v:v:v). The extract is centrifuged and an aliquot of the supernatant was partitioned using cyclohexane. An aliquot of the organic phase was evaporated to dryness and re-dissolved in a buffered ethanol:water (80:20, v/v) solution for analysis by LC/MS/MS. MS/MS detection using the positive ionization mode monitored ion transitions from m/z 388 $\rightarrow$ 194 for pyraclostrobin and m/z 358 $\rightarrow$ 164 for 500M07. Residues were quantified using external standard calibration for each analyte.

The analytical method was evaluated during each sample set by fortifying a control matrix with standards of pyraclostrobin and 500M07. The validated LOQ for residues of pyraclostrobin and its metabolite (500M07) in/on wheat RAC samples was 0.02 ppm each (0.04 ppm combined). The LOD for each analyte was 20% of the LOQ, equivalent to 0.004 ppm each.



## C. RESULTS AND DISCUSSION

The storage intervals for wheat samples from collection to extraction for analysis were 222 days (7.3 months) for forage, 210 days (6.9 months) for hay, 154 days (5.1 months) for grain, and 155 days (5.1 months) for straw (summarized in Table C.2.). Storage stability data are available indicating that residues of pyraclostrobin and its metabolite 500M07 are stable under frozen storage conditions in/on fortified samples of grape juice, sugar beet tops and root, tomatoes, and wheat grain and straw for up to 25 months (L. Cheng, DP# 269668, 11/28/01).

The analytical method (D9908) was validated at 0.02-2.0 ppm for pyraclostrobin and its metabolite in wheat RAC. Control samples were fortified with each analyte. Recoveries were within the acceptable range of 70-120%. Recoveries ranged from 66-95% (81±11%, n=4) and 74-95% (85±7%, n=4), respectively, as summarized in Table C.1.

Residue data is reported in Table C.3. The results from these analyses (forage, hay, grain and straw) indicate that combined residues of pyraclostrobin were 0.31-0.68 ppm (20 GPA), 0.19-0.70 ppm (2 GPA), and 0.30-0.71 ppm (1 GPA) in/on treated wheat forage samples, 1.00-2.20 ppm (20 GPA), 1.23-2.30 ppm (2 GPA), and 1.24-2.34 ppm (1 GPA) in/on treated wheat hay, each harvested 14 DALA. Combined residues of pyraclostrobin were 0.11 and 0.09 ppm (20 GPA), 0.15 and 0.14 ppm (2 GPA), and 0.22 and 0.15 ppm (1 GPA) in/on straw samples and were below the LOQ (<0.04 ppm) in all treated grain samples, each harvested at maturity.

Matrix	Spike level	Compound	Sample size	Recoveries	Mean ± std dev
	mg/kg	•	n	<b>%</b> ¹	%
Forage	0.02	Pyraclostrobin	1	66 [71,61]	66
	2.0		1	91 [93,90]	91
Hay	0.02		1	71 [65, 63, 85]	71
	2.0		1	89 [94, 101, 71]	89
Grain	0.02		1	77 [70, 84]	77
	2		1	95 [92, 97]	95
Straw	0.02		1	71	71
	2.0		1	87	87
	0.02, 2	Overall	8	66-95	81 ± 11
Forage	0.02	500M07	1	81	81
	2.0		1	94	94
Hay	0.02		1	74 [68, 80]	74
	2.0		1	85 [93, 78]	85
Grain	0.02		1	78 [68, 89]	78
	2		1	95 [96, 93]	95

TABLE C.1.	Summary of Met	thod Recoveries	of Pyraclostrobin	from Wheat	
Matrix	Spike level mg/kg	Compound	Sample size n	Recoveries %	Mean ± std dev %
Straw	0.02		2	83	83
	2.0		2	88	88
	0.02, 2	Overall	8	74-95	85 ± 7

<sup>&</sup>lt;sup>T</sup>Mean of multiple analyses, the values in brackets reflect the individual results.

TABLE C.2.	Summary	of Storage Conditions.		
Matrix (RAC)		Storage Temperature °C	Actual Storage Duration days	Interval of Demonstrated Storage Stability months
Forage		<-5	186-222 (6.1-7.3 months)	19-25 <sup>1</sup>
Hay			171-210 (5.6-6.9 months)	
Grain			154 (5.1 months)	
Straw			155 (5.1 months)	

L. Cheng, DP# 269668, 11/28/01

TABLE C.3.	Re	sidue Data fro	m Crop Fiel	d Trials wit	h Pyra	clostrobin			
Trial ID (City, State/Year)	Zone	Crop/ Variety	Commodity or Matrix	Total Rate lb ai/A (kg a.i./ha)	GPA <sup>1</sup>	PHI <sup>2</sup> days	Pyraclostrobin ppm	500M07 <sup>3</sup> ppm	Combined Residues ppm
(Northwood,	5	Spring	Forage	0.30 (0.336)	20	14	0.4608	0.0945	0.56
ND/2008); R080595		Wheat/Glenn	Forage				0.5725	0.1048	0.68
Roods			Hay	1			0.8168	0.1854	1.00
			Hay	1			0.9624	0.2342	1.20
			Forage	0.30 (0.336)	2	14	0.4767	0.1159	0.59
			Forage				0.4383	0.1057	0.54
			Hay	1			1.0006	0.2493	1.25
			Hay	1			0.9602	0.2717	1.23
:			Forage	0.31 (0.347)	1	14	0.5562	0.0992	0.66
			Forage				0.5675	0.1175	0.68
			Hay			}	0.9935	0.2509	1.24
			Hay			ĺ	1.0680	0.2426	1.31
(Northwood,	5	Spring	Forage	0.30 (0.336)	20	15	0.3106	0.1093	0.42
ND/2008); R080596		Wheat/Kelby	Forage	1			0.3712	0.1043	0.48
			Hay	1			1.7321	0.4711	2.20
			Hay	1			1.5574	0.4629	2.02
			Forage	0.30 (0.336)	2	15	0.4743	0.1219	0.60
			Forage	1			0.5564	0.1485	0.70
			Hay	1			1.4887	0.4391	1.93
			Hay				1.7957	0.5061	2.30
			Forage	0.30 (0.336)	1	15	0.5437	0.1343	0.68
			Forage			!	0.5550	0.1512	0.71



TABLE C.3.	Re	sidue Data fro	m Crop Fiel	d Trials wit	•				·
Trial ID (City, State/Year)	Zone	Crop/ Variety	Commodity or Matrix	Total Rate lb ai/A (kg a.i./ha)	GPA <sup>1</sup>	PHI <sup>2</sup> days	Pyraclostrobin ppm	500M07 <sup>3</sup> ppm	Combined Residues ppm
			Hay				1.6595	0.4649	2.12
			Hay				1.8541	0.4861	2.34
(Ephrata,	11	Spring	Forage	0.30 (0.336)	20	14	0.2380	0.0684	0.31
WA/2008); R080597		Wheat/DNS Solano	Forage	[ ·			0.2429	0.0800	0.32
			Hay	1			1.1197	0.3642	1.48
			Hay	]			1.3056	0.3943	1.70
			Grain	]	20	69	< 0.02	< 0.02	< 0.04
			Grain				< 0.02	< 0.02	< 0.04
			Straw				0.0757	0.0357	0.11
			Straw	1			0.0627	0.0314	0.09
			Forage	0.30 (0.336)	2	14	0.3554	0.0866	0.44
			Forage				0.1528 [0.15, 0.15] <sup>4</sup>	0.0372	0.19
			Hay				1.1215	0.3320	1.45
			Hay				1.2179	0.4237	1.64
			Grain		2	69	< 0.02	< 0.02	< 0.04
			Grain				< 0.02	< 0.02	< 0.04
			Straw				0.1103	0.0445	0.15
	[		Straw				0.0969	0.0405	0.14
			Forage	0.30 (0.336)	1	14	0.3142	0.0841	0.40
			Forage		ı		0.2287	0.0665	0.30
ŀ			Hay				1.4963	0.4235	1.92
			Hay			Ì	1.3574	0.3719	1.73
			Grain		1	69	< 0.02	< 0.02	< 0.04
			Grain				< 0.02	< 0.02	< 0.04
			Straw				0.1647	0.0545	0.22
			Straw				0.1083	0.0393	0.15

GPA = Gallons per Acre
PHI = Preharvest interval

All residues are expressed in parent equivalents.
 Mean of multiple analyses, the values in brackets reflect the individual results.



TABLE C.4		mary (	of Residue Da	ta from	Crop F	ield Tria					
Commodity	Total	PHI	Analyte					ie Levels			
:	Applic. Rate lb a.i./A	days		GPA	n¹	Min	Max	HAFT <sup>2</sup>	Median (STMdR)	Mean (STMR)	Std. Dev.
Forage	0.30	14-15	Pyraclostrobin	20	6	0.24	0.57	0.52	0.34	0.37	0.13
			500M07			0.07	0.11	0.11	0.10	0.09	0.02
			Total Pyraclostrobin			0.31	0.68	0.62	0.45	0.46	0.14
			Pyraclostrobin	2	6	0.15	0.56	0.52	0.46	041	0.14
			500M07			0.04	0.15	0.14	0.11	0.10	0.04
			Total Pyraclostrobin			0.19	0.70	0.65	0.57	0.51	0.18
			Pyraclostrobin	1	6	0.23	0.57	0.56	0.55	0.46	0.15
			500M07			0.07	0.15	0.14	0.11	0.11	0.03
	Var. 0.20 14.15		Total Pyraclostrobin			0.30	0.71	0.70	0.67	0.57	0.18
Hay	0.30	14-15	Pyraclostrobin	20	6	0.82	1.73	1.64	1.21	1.25	0.35
			500M07			0.19	0.47	0.47	0.38	0.35	0.12
			Total Pyraclostrobin			1.01	2.20	2.11	1.59	1.60	0.46
			Pyraclostrobin	2	6	0.96	1.80	1.64	1.17	1.26	0.32
			500M07			0.25	0.51	0.47	0.38	0.37	0.10
			Total Pyraclostrobin			1.23	2.30	2.12	1.55	1.63	0.42
			Pyraclostrobin	1	6	0.99	1.85	1.76	1.43	1.40	0.33
		1	500M07 Total			<0.24	0.49 2.34	0.48 2.23	0.40	0.37	0.11
		L	Pyraclostrobin								
Grain	0.30	69	Pyraclostrobin	20	2	<0.02	<0.02	<0.02	<0.02	<0.02	N/A <sup>3</sup>
			500M07			<0.02	<0.02	<0.02	<0.02	<0.02	N/A
			Total Pyraclostrobin			<0.04	<0.04	<0.04	<0.04	<0.04	N/A
			Pyraclostrobin	2	2	<0.02	<0.02	<0.02	<0.02	<0.02	N/A
			500M07 Total			<0.02	<0.02 <0.04	<0.02	<0.02 <0.04	<0.02	N/A N/A
			Pyraclostrobin Pyraclostrobin	1	2	<0.02	<0.02	<0.02	<0.02	<0.02	N/A
			500M07	•	-	<0.02	<0.02	<0.02	<0.02	<0.02	N/A
			Total Pyraclostrobin			<0.04	<0.04	<0.04	<0.04	<0.04	N/A
Straw	0.30	69	Pyraciostrobin	20	2	0.06	0.08	0.07	0.07	0.07	N/A
			500M07			0.03	0.04	0.03	0.03	0.03	N/A
			Total Pyraclostrobin			0.09	0.11	0.10	0.10	0.10	N/A
			Pyraclostrobin	2	2	0.10	0.11	0.10	0.10	0.10	N/A
		1	500M07		1	0.04	0.04	0.04	0.04	0.04	N/A

TABLE C.	4. Sum	mary	of Residue Da	ta from	Crop F	ield Tria	ls with I	yraclost	robin.		············
Commodity	Total Applic.	PHI days	Analyte					ue Levels ppm)			
	Rate lb a.i./A			GPA	n¹	Min	Max	HAFT <sup>2</sup>	Median (STMdR)	Mean (STMR)	Std. Dev.
			Total Pyraclostrobin			0.14	0.15	0.15	0.15	0.15	N/A
			Pyraclostrobin	1	2	0.11	0.16	0.14	0.14	0.14	N/A
			500M07			0.04	0.05	0.05	0.05	0.05	N/A
			Total Pyraclostrobin			0.15	0.21	0.19	0.19	0.19	N/A

<sup>&</sup>lt;sup>1</sup>n = number of individual specimens

#### D. CONCLUSION

The residues of pyraclostrobin between the various application spray volumes were comparable on all wheat RAC.

Combined residues of pyraclostrobin were 0.31-0.68 ppm (20 GPA), 0.19-0.70 ppm (2 GPA), and 0.30-0.71 ppm (1 GPA) in/on wheat forage samples; 1.00-2.20 ppm (20 GPA), 1.23-2.30 ppm (2 GPA), and 1.24-2.34 ppm (1 GPA) in/on wheat hay, each harvested 14 DALA. Combined residues of pyraclostrobin were 0.11 and 0.09 ppm (20 GPA), 0.15 and 0.14 ppm (2 GPA), and 0.22 and 0.15 ppm (1 GPA) in/on straw samples and were below the LOQ (<0.04 ppm) in all grain samples, each harvested at maturity.

Acceptable concurrent method recovery data for wheat were obtained for each analyte. The validated LOQ for residues of pyraclostrobin and 500M07 in/on wheat RAC samples was 0.02 ppm each (0.04 ppm combined).

The storage interval from collection to extraction ranged from 154-222 days (5.1-7.3 months) for wheat samples. Adequate storage stability data for pyraclostrobin and its metabolite 500M07 are available to support the storage conditions and intervals.

#### E. REFERENCES

DP #s:

269668, 272771, 272789, 274095,

274192, 274471, 274957, 275843, and 278429

Subject:

PP#0F06139. PC Code 099100. Pyraclostrobin on Various Crops: Bananas (import), Barley, Berries, Bulb Vegetables, Citrus Fruits,

Cucurbit Vegetables, Dried Shelled Pea & Bean (except Soybean),

Fruiting Vegetables, Grapes, Grass, Peanut, Pistachio, Root Vegetables (except Sugar Beet), Rye, Snap Beans, Stone Fruits,

Strawberry, Sugar Beet, Tree Nuts, Tuberous and Corm

<sup>&</sup>lt;sup>2</sup>HAFT = Highest Average Field Trial based on combined residues

 $<sup>^{3}</sup>N/A = Not applicable$ 



Vegetables, and Wheat. Review of Analytical Methods and Residue Data. EPA File Symbols: 7969-RIT, 7969-RIA. CAS

#175013-18-0.

From:

L. Cheng

To:

C. Giles-Parker/J. Bazuin

Dated:

11/28/01

MRIDs:

45118428-451184-37, 45118501-45118512, 45118514-45118537, 45118601-45118625, 45160501, 45272801, 45274901, 45321101,

45367501, 45399401, and 454299

#### F. DOCUMENT TRACKING

RDI: Meheret Negussie (11/05/09); ChemTeam (11/12/09); Stephen Funk, 11/30/09

Petition Number: N/A DP #s: 368042/368086

PC Code: 099100

Template Version June 2005.

Primary Evaluator

Meheret Negussie, Chemist

Date: 11/05/09

Risk Assessment Branch III

Health Effects Division (7509P)

Helevet kousse

Approved by

Stephen Funk, Senior Science Advisor

Date: 11/30/09

Risk Assessment Branch III

Health Effects Division (7509P)

# **STUDY REPORTS:**

47774601 Wyatt, D. (2009) Magnitude of the Residue of Pyraclostrobin in or on Sweet Corn and Field Corn Raw Agricultural Commodities Following Applications of BAS 500 00F with Various Application Spray Volumes. BASF Study Number 349588. BASF Reg. Doc. No. 2009/7000168. Unpublished study prepared by the Carringers, Inc., 134p.

# **EXECUTIVE SUMMARY:**

BASF Corporation (BASF) has submitted supplemental field trial data for pyraclostrobin (BAS 500 F) on corn. A total of three corn trials were conducted in EPA Region 5 (IL, 2-trials; IA, 1trial) during the 2008 growing season.

At each test location, an untreated plot (control) and three treated plots were established at each site. The treated plots received two foliar broadcast applications of pyraclostrobin (2 lb ai/gal EC (emulsifiable concentrate); BASF formulation code, BAS 500 00F) at 0.19-0.21 lb ai/A (0.213-0.235 kg ai/ha), with a 6-8 day retreatment interval (RTI), totaling a seasonal rate of 0.39-0.41 lb ai/A (0.437-0.460 kg ai/ha). Applications were initiated when the corn plants were at the silking to blister growth stages (BBCH 61-71). At one site (R080491), two additional broadcast applications of pyraclostrobin were made to the treated plots at 0.2 lb ai/A (0.224 kg ai/ha) resulting in four sequential applications (two times the maximum allowed per season), with a 7day RTI, totaling in a seasonal rate of 0.80-0.81 lb ai/A (0.897-0.908 kg ai/ha). The third application at this site was made at BBCH 87 to maturing corn and the fourth application was made 7 days prior to harvest of mature grain and stover (BBCH 89).

The applications were made in approximately 20-21 gal/A (GPA) of water (187-196 L/ha), 2 GPA of water (19-20 L/ha), and 1 GPA of water (9-10 L/ha) using commercial or simulated commercial ground equipment. A crop oil concentrate (COC) was added to the spray mixture for all applications at a rate of 0.5 pt/A.

Corn forage and kernel plus cob with husk removed (K+CWHR) raw agricultural commodity (RAC) samples were harvested from all three sites 6-8 days after the second application, at

BBCH 75-79 growth stage (milk stage-R3). The mature grain and stover RAC samples were harvested at normal crop maturity, 7 days after last application (DALA) at the test site in IA.

The residues of pyraclostrobin and its N-desmethoxy metabolite, 500M07, previously designated BF 500-3) in/on corn RAC samples (K+CWHR, forage, grain, and stover) were quantitated using a liquid chromatography/mass spectroscopy/mass spectroscopy (LC/MS/MS) method, BASF analytical method number D9908 (Version II). The validated limit of quantitation (LOQ) was 0.02 ppm for each analyte, for a combined LOQ of 0.04 ppm. Acceptable concurrent method recovery data for corn RAC samples were obtained for each analyte. The method limit of detection (LOD) for each analyte in/on corn RAC samples was 0.004 ppm.

The results from these analyses indicate that combined residues of pyraclostrobin were 0.64-3.26 ppm (20 GPA), <0.04-3.37 ppm (2 GPA), and 0.29-2.57 ppm (1 GPA) in/on treated corn forage samples, each harvested 6-8 DALA. Combined residues of pyraclostrobin were below the LOQ (<0.04 ppm) in all treated corn K+CWHR samples.

The results from grain and stover trials indicate that combined residues of pyraclostrobin were below the LOQ in all treated corn grain samples harvested at maturity, 7 DALA. Combined residues of pyraclostrobin in/on stover samples harvested 7 DALA were 3.22 and 3.53 ppm (20 GPA), 2.49 and 2.53 ppm (2 GPA), and 0.55 and 1.68 ppm (1 GPA).

The residues of pyraclostrobin between the various application spray volumes were comparable on all corn RACs except for stover where combined residues averaged 3.38, 2.51, and 1.12 ppm with spray volumes of 20, 2, and 1 GPA, respectively, indicating that residues are lower with lower spray volumes.

The storage interval from collection to extraction ranged from 145-219 days (4.8-7.2 months) for corn RAC samples. Adequate storage stability data are available indicating that both pyraclostrobin and BF 500-3 are stable in frozen storage for up to 25 months (L. Cheng, DP# 269668, 11/28/01).

#### STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the field trial residue data are classified as scientifically acceptable. The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document DP# 368042.

### **COMPLIANCE:**

Signed and dated Good Laboratory Practice (GLP), Quality Assurance and Data Confidentiality statements were provided. No deviations from regulatory requirements were reported which would have an impact on the validity of the study.

#### A. BACKGROUND INFORMATION

Pyraclostrobin belongs to the strobilurin class of fungicides. Strobilurins are synthetic analogs of a natural antifungal substance which inhibits spore germination, mycelial growth, and sporulation of the fungus on the leaf surface. The fungicide is currently registered to BASF for use on a variety of field, vegetable, fruit, and nut crops. Permanent tolerances are established [40 CFR §180.582(a)(1)] for the combined residues of pyraclostrobin and its desmethoxy metabolite (BF 500-3), expressed as parent, in/on numerous plant commodities at levels ranging from 0.02 ppm in/on wheat grain to 29 ppm in/on leafy vegetables, except *Brassica*. BASF has submitted label amendments for Headline® Fungicide, (EPA Reg. No. 7969-186) and Headline® SC Fungicide (EPA Reg. No. 7969-289) to add aerial application at spray volumes down to 1 GPA in corn and wheat.

The chemical structure and nomenclature of pyraclostrobin are presented in Table A.1. The physicochemical properties of the technical grade of pyraclostrobin are presented in Table A.2.

TABLE A.1. Test Comp	ound Nomenclature.
Compound	CI—NOCH <sub>3</sub>
Common name	Pyraclostrobin
Company experimental name	BAS 500 00F
IUPAC name	methyl N-{2-[1-(4-chlorophenyl)-1H-pyrazol-3-yloxymethyl]phenyl}(N-methoxy) carbamate
CAS name	methyl [2-[[[1-(4-chlorophenyl)-1 <i>H</i> -pyrazol-3-yl]oxy]methyl]phenyl]methoxycarbamate
CAS registry number	175013-18-0
End-use products (EP)	2 lb ai/gal emulsifiable concentrate formulation (EC; Headline® Fungicide, EPA Reg. No. 7969-186). 2 lb ai/gal suspension concentrate formulation (SC; Headline®SC Fungicide, EPA Reg. No. 7969-289).

Parameter	Value	References <sup>1</sup> (MRID)		
Melting point/range	63.7-65.2° C	45118213		
рН	Not applicable			
Density	1.367 g/cm <sup>3</sup>	45118214		
Water solubility at 20° C	1.9 ± 0.17 mg/L (deionized water, pH 5.8)	45118233		
Solvent solubility	n-heptane (0.37 g/100mL); 2-propanol (3.0 g/100mL); 1-octanol (2.42 g/100mL); olive oil (2.80 g/100m/L); methanol (10.08 g/100mL); >50 g/100mL in acetone, ethyl acetate, acetonitrile, DCM and toluene.	45118228		
Vapor pressure	2.6 x 10 <sup>-10</sup> hPa at 20° C	45118214		

TABLE A.2. Physicochemical Properties of Technical Grade Pyraclostrobin.									
Parameter	Value	References <sup>1</sup> (MRID)							
Dissociation constant, pK <sub>a</sub>	None (no dissociable moieties)								
Octanol/water partition coefficient, Log(K <sub>OW</sub> ) at room temperature	3.990 mean log Pow; Pow is 9772	45118215							
UV/visible absorption spectrum	The structural identity of BAS 500 F was confirmed by NMR and MS spectra. UV molecular extinction (e [1 mol <sup>-1</sup> cm <sup>-1</sup> ]): 2.5x10 <sup>4</sup> at 205 nm; 2.4x10 <sup>4</sup> at 275 nm.	1996/10955 <sup>2</sup>							

Product Chemistry data were reviewed by the Registration Division (DP#s 269848 and 274191, 5/3/01, 5/15/01, and 6/7/01, S. Malak).

### B. EXPERIMENTAL DESIGN

At each test location, an untreated plot and three treated plots were established to determine residues in side-by-side comparisons using application spray volumes of 20, 2, and 1 GPA. The treated plots received two foliar broadcast applications of an EC formulation of pyraclostrobin (2 lb ai/gal EC) at 0.19-0.21 lb ai/A (0.213-0.235 kg ai/ha), with a 6-8-day RTI, totaling a seasonal rate of 0.39-0.41 lb ai/A (0.437-0.460 kg ai/ha). The target application timing was approximately 2 weeks prior to the harvest of forage and K+CWHR, at growth stage silking to blister (BBCH 61-71; R1-R3). At one site (Iowa, R080491), two additional broadcast applications of pyraclostrobin were made to the same treated plots, at 0.2 lb ai/A (0.224 kg ai/ha), with a 7-day RTI, resulting in four sequential applications (two times the maximum allowed per season) and a seasonal rate of 0.80-0.81 lb ai/A (0.897-0.908 kg ai/ha). The third application was made 42 days after second application to maturing corn (BBCH 87, black layer, ~60% dry matter), approximately 2 weeks prior to the harvest of mature corn grain and stover and the fourth application was made 7 days prior to harvest of mature grain and stover (BBCH 89).

The applications were made in approximately 20-21 GPA of water (187-196 L/ha, Treatment 2), 2 GPA of water (19-20 L/ha, Treatment 3), and 1 GPA of water (9-10 L/ha, Treatment 4) using commercial or simulated commercial ground equipment. A COC was added to the spray mixture for all applications at a rate of 0.5 pt/A.

Single control and duplicate treated corn RAC samples were harvested (by hand or by commercial equipment) at each location. Corn forage and K+CWHR raw agricultural commodity samples were harvested from all three sites 6-8 days after the second application, at BBCH 75-79 growth stage (milk stage-R3). The mature grain and stover RAC samples were harvested at normal crop maturity, 7 DALA at the test site in IA.

## **B.1.** Study Site Information

Trial site conditions are presented in Table B.1.1. Study site information was provided, and weather data (temperature and rainfall) were compared to historical data (10 year average). The petitioner stated that the weather conditions were within normal ranges with typical

BASF registration Document Number.



variations; however, the weather did not have an impact on the study. Information on maintenance pesticides and fertilizers was also provided for each site.

TABLE B.1.1 Trial Site Conditio	ns.						
Trial Identification (City, State/Year)	Soil characteristics						
	Туре	%OM	pН	CEC meq/g			
R080489 (Carlyle, IL/2008)	Silt Loam	2.12	6.04	11.51			
R080490 (Wyoming, IL/2008)	Silt Loam	3.6	6.8	13.3			
R080491 (Richland, IA/2008)	Silty Clay Loam	4.3	6.48	25.7			

Location	EP1		App	lication				Tank Mix	
(City, State/Year); Trial ID		Treatment No.	Method/Timing <sup>2</sup>	Volume GPA <sup>3</sup> (L/ha) <sup>4</sup>	Rate Ib a.i./A (kg a.i./ha)	RTI <sup>5</sup> days	Total Rate lb a.i./A (kg a.i./ha)	Adjuvants	
(Carlyle, IL/2008);	Headline® Fungicide			20 (187)	0.20 (0.224)	NA	0.40 (0.448)	COC 0.5 pt/A	
R080489	2 lb ai/gal	2	Foliar Broadcast/BBCH 73	21 (196)		8		-	
	EC	3	Foliar Broadcast/BBCH 61-73	2.0 (19)	0.20	NA	0.40		
		3	Foliar Broadcast/BBCH 73	2.0 (19)	(0.224)	8	(0.448)		
		4	Foliar Broadcast/BBCH 61-73	1.0 (9)	0.20	NA	0.40		
		4	Foliar Broadcast/BBCH 73	1.1 (10)	(0.224)	8	(0.448)		
(Wyoming, IL/	Headline® Fungicide	2	Foliar Broadcast/BBCH 61-65	21 (196)	0.20-0.21 (0.224-	NA	0.41 (0.460)	COC 0.5 pt/A	
2008); R080490	2 lb ai/gal EC	2	Foliar Broadcast/BBCH 73	21 (196)	0.235)	6	(	•	
		3	Foliar Broadcast/BBCH 61-65	2.1 (20)	0.20	NA	0.40		
		3	Foliar Broadcast/BBCH 73	2.0 (19)	(0.224)	6	(0.448)		
		Ţ	4	Foliar Broadcast/BBCH 61-65	1.0 (9)	0.19-0.20	NA	0.39	
		4	Foliar Broadcast/BBCH 73	1.0 (9)	(0.213- 0.224)	6	(0.437)		
(Richland,	Headline®	2	Foliar Broadcast/BBCH 71	20 (187)	0.20	NA	0.40	COC	
IA/2008); R080491	Fungicide 2 lb ai/gal	2	Foliar Broadcast/BBCH 73	20 (187)	(0.224)	8	(0.448)	0.5 pt/A	
	EC	2	Foliar Broadcast/BBCH 87	20 (187)	0.20	(42) 5	0.80		
		2	Foliar Broadcast/BBCH 89	20 (187)	(0.224)	7	(0.897)		
		3	Foliar Broadcast/BBCH 71	2.0 (19)	0.20	NA	0.40		
		3	Foliar Broadcast/BBCH 73	2.0 (19)	(0.224)	8	(0.448)		
		3	Foliar Broadcast/BBCH 87	2.0 (19)	0.20	(42) <sup>5</sup>	0.80		
		3	Foliar Broadcast/BBCH 89	2.0 (19)	(0.224)	7	(0.897)		
		4	Foliar Broadcast/BBCH 71	1.0 (9)	0.20-0.21	NA	0.41		
		4	Foliar Broadcast/BBCH 73	1.0 (9)	(0.224- 0.235)	8	(0.460)		
		4	Foliar Broadcast/BBCH 87	1.0 (9)	0.20	(42) 5	0.81		
			Foliar Broadcast/BBCH 89	1.0 (9)	(0.224)	7	(0.908)		

EP = End-use Product

<sup>&</sup>lt;sup>2</sup> BBCH = Monograph Growth Stages of Plants

<sup>&</sup>lt;sup>3</sup> GPA = Gallons per Acre

<sup>&</sup>lt;sup>4</sup> L/ha = Liters/hectare

<sup>&</sup>lt;sup>5</sup> RTI = Retreatment Interval; the value in parentheses reflect the RTI between the early season applications and the late season applications (42 days).

	Swee	t Corn	Field	Corn
NAFTA Growing Zones	Submitted	Requested	Submitted	Requested
1		2		1
1A				
2		1		1
3		1		
4				
5	3	5	1	17
5A				
5B				
6				1
7				
7A				
8				
9				
10		1		•
11		1		
12		1		
13				
14				:
15				
16				
17				
18				
19				
20				
21				
Total	3	12	1	20

Justification for the number of side-by-side bridging trials was discussed with EPA officials prior to the start of the study (Rick Loranger, November 2007).

#### **B.2.** Sample Handling and Preparation

Single control and duplicate treated samples were collected from each test site. All corn RAC samples were placed in freezers within 1.6 hours after collection from the field. All samples were maintained frozen at the field facilities and were shipped 6-15 days later by ACDS freezer truck to the analytical laboratory, BASF Agricultural Research Center (ARC) (Research Triangle Park, NC).

All corn RAC samples were received frozen from the field and were stored in a freezer (<-5°C) at BASF ARC. Samples were homogenized (with dry ice) and were stored frozen in plastic bags prior to analysis. All processed samples were stored frozen until used for fortification and/or analysis.

# **B.3.** Analytical Methodology

The corn RAC samples (K+CWHR, forage, grain, and stover) were analyzed for residues of pyraclostrobin using BASF Analytical Method Number D9908 (Version II), entitled "Method for Determination of BAS 500 F, BF 500-3, and BAS 510 F Residues in Plant Matrices using LC/MS/MS" (Reference 1).

Briefly, corn samples ~5g were extracted with methanol:water:2N HCl (70:25:5, v:v:v). The extract was centrifuged and an aliquot of the supernatant was partitioned using cyclohexane. An aliquot of the organic phase was evaporated to dryness and re-dissolved in a buffered methanol:water (80:20, v/v) solution for analysis by LC/MS/MS. MS/MS detection using the positive ionization mode monitored ion transitions from m/z 388 $\rightarrow$ 194 for pyraclostrobin and m/z 358 $\rightarrow$ 164 for 500M07. Residues were quantified using external standard calibration for each analyte.

The performance of the analytical method was evaluated during each sample set by fortifying control matrix with standards of pyraclostrobin and 500M07. The validated LOQ for residues of pyraclostrobin and its metabolite (500M07) in/on corn RAC samples was 0.02 ppm each (0.04 ppm combined). The LOD for each analyte was 20% of the LOQ, equivalent to 0.004 ppm each.

#### C. RESULTS AND DISCUSSION

The storage intervals for corn samples from collection to extraction for analysis ranged from 196-218 days (6.4-7.2 months) for forage, 197-219 days (6.5-7.2 months) for K+CWHR, 145-146 days (4.8 months) for grain, and 165-169 days (5.4-5.6 months) for stover (summarized in Table C.2.). Storage stability data are available indicating that residues of pyraclostrobin and its metabolite 500M07 are stable under frozen storage conditions in/on fortified samples of grape juice, sugar beet tops and root, tomatoes, and wheat grain and straw for up to 25 months (L. Cheng, DP# 269668, 11/28/01).

The analytical method (D9908) was validated at 0.02 -20 ppm for pyraclostrobin and its metabolite in corn RAC. Control samples were fortified with each analyte. Recoveries were within the acceptable range of 70-120%. Recoveries for pyraclostrobin and 500M07 ranged from 76-99% (86±7%, n=12) and 72-101% (82±8%, n=12), respectively, as summarized in Table C.1.

Residue data are reported in Table C.3. The results from these analyses indicate that combined residues (parent and metabolite) ranged from 0.64-3.26 ppm (20 GPA), <0.04-3.37 ppm (2 GPA), and 0.29-2.57 ppm (1 GPA) in/on forage and were below the LOQ (<0.04 ppm combined) for K+CWHR following two foliar applications of pyraclostrobin at 0.2 lb ai/A, harvested at the milk stage, 6-8 DALA.

Combined residues of pyraclostrobin were 3.22 and 3.53 ppm (20 GPA), 2.49 and 2.53 ppm (2 GPA), and 0.55 and 1.68 ppm (1 GPA) for corn grain and were below the LOQ (<0.04 ppm

combined) for corn stover following four foliar applications of pyraclostrobin at 0.2 lb ai/A, in all samples harvested at maturity from each of the treated plots, at 7 DALA.

TABLE C.1.		thod Recoveries o			
Matrix	Spike level	Compound	Sample size	Recoveries	Mean ± std dev
	mg/kg		n	% <sup>1</sup>	%
Forage	0.02	Pyraclostrobin	2	84 [88, 80]; 87	86
	20		2	76 [76, 77]; 91	84
K+CWHR	0.02		1	76	76
	20		1	83	83
Grain	0.02		1	83 [73,92]	83
	2		1	93 [99, 86]	93
Stover	0.02		2	93 [84, 101]; 83 [84, 82, 84]	88
	20		2	83 [81, 86]; 99 [106, 92]	91
Forage	0.02	500M07	2	72 [81, 63]; 82	77
	20		2	76 [79, 72]; 77	77
K+CWHR	0.02		1	75	75
	20		1	86	86
Grain	0.02		1	90 [85, 95]	90
	2		1	86 [91, 82]	86
Stover	0.02		2	84 [82, 85]; 76 [77, 75, 75]	80
	20		2	83 [84, 83]; 101 [95, 107]	92

The values in brackets reflect the individual results for multiple analyses of the same fortification sample. In these cases, the mean of all the results appears outside of the brackets.

TABLE C.2. Sumr	nary of Storage Conditions.		
Matrix (RAC)	Storage Temperature °C	Actual Storage Duration days	Interval of Demonstrated Storage Stability months
Forage	<-5	196-218 (6.4-7.2 months)	19-25 <sup>1</sup>
K+CWHR	·	197-219 (6.5-7.2 months)	1
Grain		145-146 (4.8 months)	
Stover		165-169 (5.4-5.6 months)	

L. Cheng, DP# 269668, 11/28/01



Trial ID	Zone	Crop/ Variety	Commodity	Total Rate	GPA <sup>1</sup>	PHI <sup>2</sup>	500	500M07 <sup>3</sup>	Combine
(City,			or Matrix	lb ai/A		days	ppm	ppm	Residues
State/Year) R080489;	5	Corn/Burrus	Forage	(kg a.i./ha) 0.40 (0.448)	20-21	6	2.44	0.69	ppm 3.13
(Carlyle,		616XLR	Forage	0.40 (0.440)	20-21	Ü	2.68	0.58	3.26
IL/2008)			K+CWHR	0.40 (0.448)			<0.02	<0.02	<0.04
				0.40 (0.448)					
			K+CWHR	0 10 (0 (10)			<0.02	<0.02	<0.04
			Forage Forage	0.40 (0.448)	2	6	2.13	0.40	2.54 3.37
			K+CWHR	0.40 (0.448)			<0.02	<0.02	<0.04
			K+CWHR	0.40 (0.440)			<0.02	<0.02	<0.04
				0.40.(0.449)	<del> </del>	6		ļ	
			Forage Forage	0.40 (0.448)	1	0	2.09	0.29	1.72 2.57
			K+CWHR	0.40 (0.448)			<0.02	<0.02	<0.04
			K+CWHR	0.10 (0.110)			<0.02	<0.02	<0.04
R080490;	5	Corn/DKC60-18	Forage	0.41 (0.460)	21	8	0.50	0.154	0.64
(Wyoming,			Forage	•••• (••••)	-	-	0.62	0.184	0.80
IL/2008)			K+CWHR	0.41 (0.460)			<0.02	<0.02	<0.04
			K+CWHR	5.11 (61.66)			<0.02	<0.02	<0.04
			Forage	0.40 (0.448)	2	8	0.71	0.224	0.93
			Forage			_	0.92	0.244	1.16
			K+CWHR	0.40 (0.448)			<0.02	<0.02	<0.04
			K+CWHR				<0.02	<0.02	<0.04
			Forage	0.39 (0.437)	1	8	0.60	0.164	0.76
			Forage	1			0.72	0.214	0.93
			K+CWHR	0.39 (0.437)			<0.02	<0.02	<0.04
			K+CWHR	1			<0.02	<0.02	<0.04
R080491;	5	Corn/Pioneer	K+CWHR	0.40 (0.448)	20	7	< 0.02	<0.02	<0.04
(Richland,		33T56	K+CWHR	1			<0.02	<0.02	<0.04
IL/2008)			Forage	0.40 (0.448)			0.84	0.20⁴	1.04
			Forage	1			0.83	0.224	1.04
			Grain	0.80 (0.897)			<0.025	<0.025	<0.04
			Grain				<0.025	<0.025	<0.04
			Stover	0.80 (0.897)			2.76	0.77	3.53
			Stover	1			2.47	0.76	3.22
			K+CWHR	0.40 (0.448)	2	7	<0.02	<0.02	<0.04
			K+CWHR	1			<0.02	<0.02	<0.04
			Forage	0.40 (0.448)	[		<0.025	<0.025	<0.04
			Forage	1			<0.025	<0.025	<0.04
			Grain	0.80 (0.897)			<0.025	<0.025	< 0.04



TABLE C.3.	Res	idue Data from	Crop Field	Trials with Py	yraclost	robin.			
Trial ID	Zone	Crop/ Variety	Commodity	Total Rate	GPA <sup>1</sup>	PHI <sup>2</sup>	500	500M07 <sup>3</sup>	Combined
(City,			or Matrix	lb ai/A		days	ppm	ppm	Residues
State/Year)				(kg a.i./ha)				<u> </u>	ppm
			Grain				<0.025	<0.025	<0.04
			Stover	0.80 (0.897)			2.13	0.36	2.49
			Stover				2.16	0.38	2.53
			K+CWHR	0.41 (0.460)	1	7	<0.02	<0.02	<0.04
			K+CWHR				<0.02	<0.02	<0.04
			Forage	0.41 (0.460)			0.42	0.084	0.51
	1		Forage				0.24	0.054	0.29
			Grain	0.81 (0.908)			<0.025	<0.025	<0.04
			Grain				<0.025	<0.025	<0.04
	1		Stover	0.81 (0.908)			1.444	0.244	1.68
			Stover				0.45 <sup>4</sup>	0.094	0.55

TABLE C.			of Residue Da	ta irom	Crop r	ieia i ria			rodin.		
Commodity	Total	PHI	Analyte					ue Levels			
	Applic. Rate lb a.i./A	days		GPA	n <sup>1</sup>	Min	Max	HAFT <sup>2</sup>	Median (STMdR)	Mean (STMR)	Std. Dev
Forage	0.39-0.41	6-8	Pyraclostrobin	20	6	0.50	2.68	2.56	0.84	1.32	0.97
		[				0.15	0.69	0.64	0.21	0.34	0.23
			Total Pyraclostrobin			0.64	3.26	3.20	1.04	1,65	1,21
			Pyraclostrobin	2	6	<0.02	2.72	2.43	0.82	1.09	1.11
		Ĭ	500M07			<0.02	0.65	0.53	0.23	0.26	0.24
			Total Pyraclostrobin			<0.04	3.37	2.96	1.05	1.35	1.35
			Pyraclostrobin	1	6	0.24	2.09	1.76	0.66	0.92	0.70
			500M07			0.05	0.48	0.39	0.19	0.21	0.16
			Total Pyraclostrobin			0.29	2.57	2.15	0.85	1.13	0.86
K+CWHR	0.39-0.41	6-8	Pyraclostrobin	20	6	<0.02	<0.02	<0.02	<0.02	<0.02	N/A <sup>3</sup>
			500M07			<0.02	<0.02	<0.02	<0.02	<0.02	N/A
			Total Pyraclostrobin			<0.04	<0.04	<0.04	<0.04	<0.04	N/A
			Pyraclostrobin	2	6	<0.02	<0.02	<0.02	<0.02	<0.02	N/A
			500M07			<0.02	<0.02	<0.02	<0.02	<0.02	N/A
			Total Pyraclostrobin			<0.04	<0.04	<0.04	<0.04	<0.04	N/A
			Pyraclostrobin	1	6	<0.02	<0.02	<0.02	<0.02	<0.02	N/A

<sup>&</sup>lt;sup>1</sup> GPA = Gallons per Acre
<sup>2</sup> PHI = Preharvest interval
<sup>3</sup> All residues are expressed in parent equivalents
<sup>4</sup> The mean of multiple analyses
<sup>5</sup> Analysed multiple times

Commodity	Total	PHI	Analyte				Residu	e Levels			
	Applic.	days						ppm			
	Rate lb a.i./A			GPA	n¹	Min	Max	HAFT <sup>2</sup>	Median (STMdR)	Mean (STMR)	Std. Dev
			500M07			<0.02	<0.02	<0.02	<0.02	<0.02	N/A
			Total Pyraclostrobin			<0.04	<0.04	<0.04	<0.04	<0.04	N/A
Grain	0.80-0.81	7	Pyraclostrobin	20	2	<0.02	<0.02	<0.02	<0.02	<0.02	N/A
			500M07			<0.02	<0.02	<0.02	<0.02	<0.02	N/A
			Total Pyraclostrobin			<0.04	<0.04	<0.04	<0.04	<0.04	N/A
			Pyraclostrobin	2	2	<0.02	<0.02	<0.02	<0.02	<0.02	N/A
			500M07			<0.02	<0.02	<0.02	<0.02	<0.02	N/A
			Total Pyraclostrobin			<0.04	<0.04	<0.04	<0.04	<0.04	N/A
			Pyraclostrobin	1	2	<0.02	<0.02	<0.02	<0.02	<0.02	N/A
			500M07			<0.02	<0.02	<0.02	<0.02	<0.02	N/A
			Total Pyraclostrobin			<0.04	<0.04	<0.04	<0.04	<0.04	N/A
Stover	0.80-0.81	7	Pyraclostrobin	20	2	2.47	2.76	2.62	2.62	2.62	N/A
			500M07			0.76	0.77	0.77	0.77	0.77	N/A
			Total Pyraclostrobin			3.22	3.53	3.38	3.38	3.38	N/A
			Pyraclostrobin	2	2	2.13	2.16	2.15	2.15	2.15	N/A
			500M07			0.36	0.38	0.37	0.37	0.37	N/A
	•		Total Pyraclostrobin			2.49	2.53	2.51	2.51	2.51	N/A
			Pyraclostrobin	ì	2	0.45	1.44	0.95	0.95	0.95	N/A
			500M07			0.09	0.24	0.17	0.17	0.17	N/A
			Total Pyraclostrobin			0.55	1.68	1.12	1.12	1.12	N/A

<sup>&</sup>lt;sup>1</sup>n = number of individual specimens

#### D. CONCLUSION

The residues of pyraclostrobin between the various application spray volumes were comparable on all corn RAC except for stover where combined residues averaged 3.38, 2.51, and 1.12 ppm with spray volumes of 20, 2, and 1 GPA, respectively, indicating that residues are lower with lower spray volumes.

Combined residues of pyraclostrobin were 0.64-3.26 ppm (20 GPA), <0.04-3.37 ppm (2 GPA), and 0.29-2.57 ppm (1 GPA) in/on treated corn forage samples, each harvested 6-8 DALA. Combined residues of pyraclostrobin were below the LOQ (<0.04 ppm) in all treated corn K+CWHR samples.

<sup>&</sup>lt;sup>2</sup>HAFT = Highest Average Field Trial based on combined residues

 $<sup>^{3}</sup>N/A = Not applicable$ 

Combined residues of pyraclostrobin were below the LOQ in all treated corn grain samples harvested at maturity, 7 DALA. Combined residues of pyraclostrobin in/on stover samples harvested 7 DALA were 3.22 and 3.53 ppm (20 GPA), 2.49 and 2.53 ppm (2 GPA), and 0.55 and 1.68 ppm (1 GPA).

Acceptable concurrent method recovery data for corn were obtained for each analyte. The validated LOQ for residues of pyraclostrobin and 500M07 in/on corn RAC samples was 0.02 ppm each (0.04 ppm combined).

The storage interval of corn samples from collection to analysis ranged from 145-219 days (4.8-7.2 months). Adequate storage stability data for pyraclostrobin and its metabolite 500M07 are available to support the storage conditions and intervals of samples from the field trials on corn.

#### E. REFERENCES

DP #s:

269668, 272771, 272789, 274095,

274192, 274471, 274957, 275843, and 278429

Subject:

PP#0F06139. PC Code 099100. Pyraclostrobin on Various Crops:

Bananas (import), Barley, Berries, Bulb Vegetables, Citrus Fruits, Cucurbit Vegetables, Dried Shelled Pea & Bean (except Soybean),

Fruiting Vegetables, Grapes, Grass, Peanut, Pistachio, Root Vegetables (except Sugar Beet), Rye, Snap Beans, Stone Fruits,

Strawberry, Sugar Beet, Tree Nuts, Tuberous and Corm Vegetables, and Wheat. Review of Analytical Methods and Residue Data. EPA File Symbols: 7969-RIT, 7969-RIA. CAS

#175013-18-0.

From:

L. Cheng

To:

C. Giles-Parker/J. Bazuin

Dated:

11/28/01

MRIDs:

45118428-451184-37, 45118501-45118512, 45118514-45118537,

45118601-45118625, 45160501, 45272801, 45274901, 45321101,

45367501, 45399401, and 454299

DP #s:

D281042, D286732, D287729, D288459, D290342, D290343, D290369,

D292440, D293088, D293684, D295893, and D298178

Subject:

Pyraclostrobin. PP#3F06581, 2F06431, 2E6473, 3E6548, 3E6553, 3E6774, and 2F06139. Petitions for the establishment of permanent tolerances to allow uses on corn (field, sweet, and pop), hops, mint, pome fruits, edible-podded legume vegetables, succulent peas, sunflower, Brassica leafy greens, soybeans, succulent beans, broccoli, cabbage, lettuce (head and leaf), spinach, celery, turnip greens, and the import commodities mango and papaya. Application for amended Section 3 registration for citrus (reduced PHI). Petitioner's response to data deficiencies identified in PP#0F06139 regarding storage stability data, dried shelled peas and



Pyraclostrobin/PC Code 099100/BASF Corporation/7969

DACO 7.4.1/7.4.2/OPPTS 860.1500/OECD IIA 6.3.1, 6.3.2, 6.3.3 and IIIA 8.3.1, 8.3.2, 8.3.3 Crop

Field Trial/Residue Decline -- Corn

beans (reduced PHI), and uses on dry and succulent peas. Summary of Analytical

Chemistry and Residue Data.

L. Cheng From:

To: C. Giles-Parker/J. Bazuin

Dated: 7/26/04

45596211, 45623406, 45623407, 45623408, 45623410, 45645801, 45645802, MRIDs:

> 45645803, 45645804, 45702901, 45765401, 45832001, 45858801, 45858802, 45903601, 45903602, 46033901-04, 46084401-04, 46109101, 46109102

#### F. **DOCUMENT TRACKING**

RDI: Meheret Negussie (11/5/09); RAB3 ChemTeam (11/12/09); Stephen Funk (11/30/09)

Petition Number: N/A DP #s: 368042/368086 PC Code: 099100

Template Version June 2005.

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